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Protonic conduction in oxide glasses: Simple relations between electrical conductivity, activation energy, and the O—H bonding state

Yoshihiro Abe, Hideo Hosono, and Yoshio Ohta
Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

L. L. Hench
University of Florida, Advanced Materials Research Center, One Progress Blvd., No. 14, Alachua, Florida 32615

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Simple relations between protonic conductivity (σ) and the peak wave number (ν_{OH}) of O-H infrared absorption band, and between activation energy for the electrical conduction and the wave number (ν_{OH}) were found in oxide glasses containing no alkali- and/or transition-metal ions. The present investigation enables one to evaluate the protonic conductivity and the activation energy at a unit proton concentration of a given glass specimen from an ir spectrum of the glass plate, respectively.

Protonic conduction in glasses has received new interest as the search for developing fast proton conductive glasses for a solid electrolyte for H_2-O_2 fuel cell and for a H_2-gas sensor has attracted much attention. In most oxide glasses, electric charge carriers are mobile monovalent cations such as alkali ions, Ag^+ and Tl^+,[1] or electrons in glasses containing multivalent transition-metal ions. Protons or water in glasses was first studied extensively by Scholze.[2] Proton conduction in crystalline solids was reviewed[3,4] and some fast proton conducting hydrated solids were reported.[5] No systematic investigation on proton conduction in glasses has so far been carried out. It is very important to clarify the characteristics on protonic conduction in glasses not only from the viewpoint of basic science but also from a practical view point of developing fast-proton-conducting glasses. Generally, it has been accepted that proton in oxide glasses is much less mobile than alkali ions; for example, Doremus[6] estimated in silica glass that the mobility of impurity Na^+ is 10^4 times as large as that of impurity H^+. This may be true in silica glass, because O—H bonding in silica glass is very strong ($\nu_{\mathrm{OH}} = 3700\ \mathrm{cm}^{-1}$).[2] In contrast with silica glass, O—H bonding in phosphate glasses ($\nu_{\mathrm{OH}} = 2600$–$3400\ \mathrm{cm}^{-1}$) is generally weak owing to the formation of hydrogen bonding: In oxide glasses, hydroxyl groups attaching to a network-forming cation (X) such as Si^{4+}, P^{5+}, and B^{3+} form a hydrogen bonding with a counter oxygen (X—O—$H \cdots$ O—X). The strength of the hydrogen bonding is controlled primarily by the type of the counter oxygen;[2] hydrogen bonding force is extremely weak for the case where the counter oxygen is of a bridging type (X—O—X) compared with where the counter is of a nonbridging type (X—O^-). The type of network modifying cations also modifies the hydrogen-bonding strength. The above-mentioned fact strongly suggests that H^+ in phosphate glasses is much more mobile rather than Na^+. In a previous paper,[7] we reported that electrical conductivity in calcium metaphosphate glasses is proportional to the square of the proton concentration as in Eq. (1).

$$\sigma = A_0[H^+]^2 \tag{1}$$

($\log_{10}\sigma = \log_{10}A_0 + 2\log_{10}[H^+]$ Eq. (1) of Ref. 1), where σ is dc electrical conductivity in S/cm at a constant temperature; $[H^+]$ is proton concentration in mol/l; and A_0 is a constant depending on the host glass. The constant A_0 is a measure of proton mobility.

It is known that electrical conductivity depends on temperature as shown by Eq. (2) and on the number (N) of electric charge carriers per unit volume by Eq. (3);

$$\sigma = \sigma_0 \exp(-E_{\mathrm{dc}}/RT)\,, \tag{2}$$

$$\sigma = Nze\mu\,, \tag{3}$$

where E_{dc} is the apparent activation energy for dc electrical conduction; R is the gas constant; T is temperature in degrees K; σ_0 is the preexponential term called frequency factor; z is the charge number (for proton $z = 1$); e is the electronic charge; and μ is mobility. Combining Eqs. (1) and (3), Eq. (4) is obtained. This equation shows that the proton mobility increases linearly with proton concentration in the calcium metaphosphate glasses on the assumption that all protons are mobile charge carriers:

$$\mu = \frac{A_0[H^+]}{e}\,. \tag{4}$$

Figure 1 shows plots of conductivity data in various alkaline-earth phosphate glasses at a constant temperature of 417 K (σ_{417}) against proton concentration. The concentration of proton $[H^+]$ was determined by using ir spectroscopy as in the previous paper.[7] As in 50CaO-$50P_2O_5$ glasses previously reported,[7] it was found that Eq. (1) holds also for these glasses. The glasses were prepared by melt-quenching technique using Pt crucibles. The starting materials used were reagent grade chemicals such as metal carbonates, metal oxides, H_3PO_4 and H_3BO_3. To control the state of dehydration, the glasses were melted

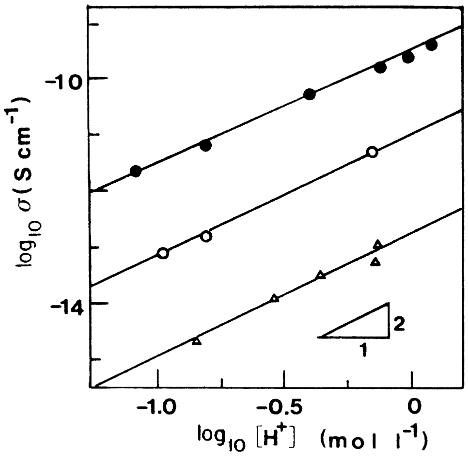

FIG. 1. Relation between electrical conductivity (σ at 417 K) and proton concentration $[H^+]$ in $45M$O-$55P_2O_5$ glasses. △, $M = $Mg; ○, $M = $Ca; ●, $M = $Ba.

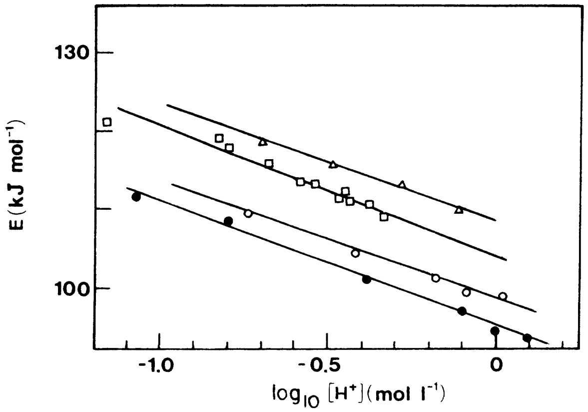

FIG. 3. Activation energy for electrical conduction (E) vs $\log_{10}[H^+]$ in glasses. △, $45MgO$-$55P_2O_5$; □, $50CaO$-$50P_2O_5$; ○, $45CaO$-$55P_2O_5$; ●, $45BaO$-$55P_2O_5$.

at 1000–1450 °C for various times depending on the compositions. Table I summarizes electrical conductivity data with ν_{OH} and $[H^+]$ for approximately 70 kinds of oxide glasses which were all measured by us. On the assumption that Eq. (1) holds for all these glasses, the values of A_0 were calculated for these glasses. Figure 2 shows the correlation of ν_{OH} and A_0. It is evident that $\log_{10}A_0 (= \sigma_{417}/[H^+]^2)$ decreases linearly with increasing ν_{OH} (Fig. 2); the relation is expressed by Eq. (5):

$$\log_{10}A_0 = -0.00937\nu_{OH} + 17.1 . \qquad (5)$$

Let us compare proton mobility in SiO_2 glass with that in a $BaOP_2O_5$ glass at a unit concentration of proton, $[H^+] = 1$ mol/l. The former is obtained by substituting $\nu_{OH} = 3700$ cm^{-1} for silica glass into Eq. (5), resulting in a very small value which is equal to 10^{-8} times the latter (barium phosphate glass). One can quantitatively understand from Eq. (5) why H^+ in silica glass is not mobile but, in phosphate glasses it is very mobile. The conductivity of alkaline-earth phosphate glasses containing both H^+ and Na^+ depends on $[H^+]$ but not on $[Na^+]$, even when $[H^+]$ is much less than $[Na^+]$.[8]

Next we will discuss how the activation energy for electrical conduction depends on the bonding strength between charge carrier and oxygen in oxide glasses. This is a very important problem from the viewpoint of basic science but any quantitative relation has not been known yet in glasses. Experimentally Eq. (6) was found to hold for $CaOP_2O_5$ glasses:

$$E = 105 - 16\log_{10}[H^+] . \qquad (6)$$

Figure 3 shows the relation between the activation energy

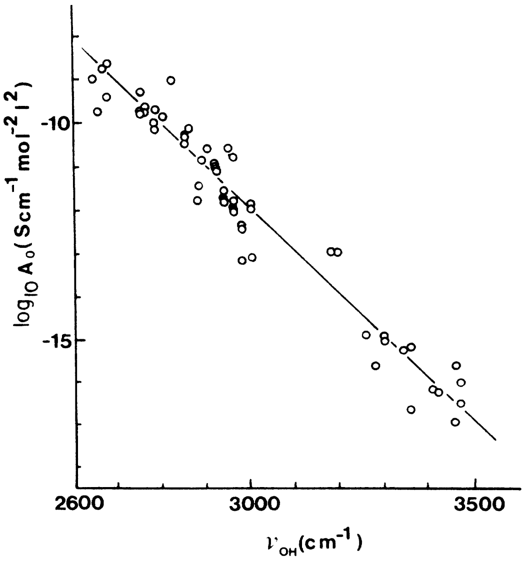

FIG. 2. Plot of A_0 (at 417 K) in Eq. (1) vs peak wave number (ν_{OH}) of ir absorption band due to OH of the glasses in Table I.

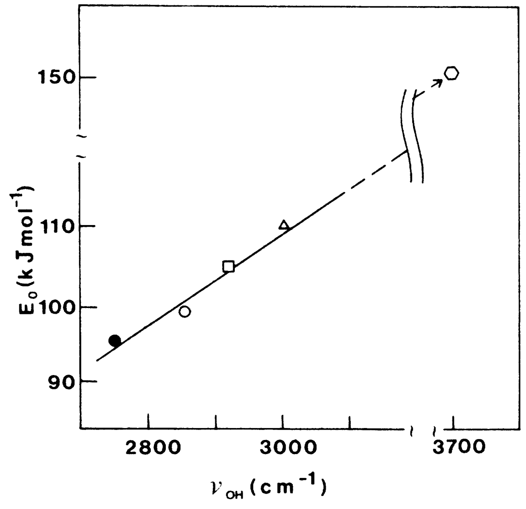

FIG. 4. Plot of E_0 in Eq. (11) vs ν_{OH} in glasses. △, $45MgO$-$55P_2O_5$; □, $50CaO$-$50P_2O_5$; ○, $45CaO$-$55P_2O_5$; ●, $45BaO$-$55P_2O_5$; ○, SiO_2 glass obtained by extrapolation.

TABLE I. Electrical conductivity data (dc) of glasses.

Glass No.	Composition	OH peak (cm^{-1}) ν_{OH}	$[H^+]$ content (mol/l)	$\log_{10}\sigma$ at $10^3/T=2.4$ ($T=417$ K) ($S cm^{-1}$)	$\log_{10}\sigma$	$\log_{10}A_0$ at $10^3/T=23$ ($T=417$ K)	E (kJ/mol)
1-1	60BeO-40P_2O_5	3360	0.20	−16.54	−2.26	−15.14	132
2-1	56BeO-44P_2O_5	3360	0.38	−17.54	−1.20	−16.70	130
3-1	50BeO-50P_2O_5	3260	0.28	−16.01	−2.55	−14.90	107
4-1	50MgO-50P_2O_5	3190	0.16	−14.55	1.17	−12.96	125
4-2	50MgO-50P_2O_5	3180	0.16	−14.56	1.18	−12.97	125
5-1	45MgO-55P_2O_5	3000	0.08	−14.17	2.65	−11.98	134
5-2	45MgO-55P_2O_5	3000	0.18	−13.36	2.55	−11.87	125
6-1	40MgO-60P_2O_5	2880	0.50	−12.07	1.99	−11.47	112
6-2	40MgO-60P_2O_5	2880	0.50	−12.43	2.02	−11.83	115
7-1	50CaO-50P_2O_5	2920	0.46	−11.67	2.06	−10.99	109
7-2			0.42	−11.76	2.18	−11.00	110
7-3			0.37	−11.88	2.16	−11.02	111
7-4			0.36	−11.90	2.26	−11.00	112
7-5			0.34	−11.90	2.13	−10.96	112
7-6			0.29	−12.02	2.37	−10.94	113
7-7			0.26	−12.09	2.18	−10.91	114
7-8			0.21	−12.38	2.13	−11.02	116
7-9			0.16	−12.69	2.18	−11.08	118
7-10			0.15	−12.78	2.16	−11.11	119
7-11			0.07	−13.32	1.75	−11.06	121
8-1	45CaO-55P_2O_5	2850	0.86	−10.61	2.69	−10.48	106
8-2			0.74	−10.50	2.29	−10.24	102
8-3			0.68	−10.61	2.40	−10.28	104
8-4			1.16	−9.54	2.29	−9.67	95
8-5			1.16	−10.02	2.60	−10.15	101
8-6			0.66	−10.39	2.16	−10.03	100
9-1	50CaO-2.5Al_2O_3-47.5P_2O_5	2940	0.54	−12.38	2.22	−11.84	116
9-2			0.38	−12.62	2.17	−11.77	118
9-3			0.32	−12.67	2.08	−11.67	118
9-4			0.27	−12.88	2.06	−11.74	120
9-5			0.24	−12.90	2.18	−11.67	125
9-6			0.18	−13.04	2.16	−11.57	121
9-7			0.14	−13.52	1.99	−11.80	126
10-1	50CaO-5Al_2O_3-45P_2O_5	2960	0.25	−13.00	2.14	−11.79	125
10-2			0.24	−13.22	2.34	−11.97	125
10-3			0.19	−13.45	2.10	−12.02	127
10-4			0.15	−13.62	1.85	−11.98	126
10-5			0.13	−13.83	2.02	−12.06	128
10-6			0.10	−14.03	1.88	−12.05	130
11-1	50SrO-50P_2O_5	2890	0.10	−12.86	2.57	−10.86	123
12-1	45SrO-55P_2O_5	2760	0.34	−10.71	2.27	−9.77	103
12-2		2750	0.16	−11.29	2.53	−9.70	110
13-1	40SrO-60P_2O_5	2670	0.52	−9.99	2.25	−9.42	97
13-2		2650	0.48	−10.38	2.22	−9.74	100
14-1	50BaO-50P_2O_5	2860	0.10	−12.13	2.65	−10.13	118
14-2		2820	0.10	−10.98	2.32	−8.98	106
14-3		2800	0.24	−11.06	2.19	−9.82	106
15-1	45BaO-55P_2O_5	2760	0.76	−9.89	2.57	−9.65	99
15-2		2750	0.68	−9.59	2.77	−9.26	99
15-3		2750	0.46	−10.43	2.39	−9.76	102

TABLE I. *(Continued).*

Glass No.	Composition	OH peak (cm^{-1}) ν_{OH}	$[H^+]$ content (mol/l)	$\log_{10}\sigma$ at $10^3/T=2.4$ ($T=417$ K) ($S\,cm^{-1}$)	$\log_{10}\sigma$	$\log_{10}A_0$ at $10^3/T=24$ ($T=417$ K)	E (kJ/mol)
16-1	$40BaO\text{-}60P_2O_5$	2670	0.94	−8.64	3.82	−8.59	99
16-2		2660	1.00	−8.72	3.54	−8.72	97
16-3		2640	0.74	−9.25	3.11	−8.99	99
17-1	$50Ca(PO_3)_2\text{-}50La(PO_3)_3$	2900	0.24	−11.82	1.79	−10.58	108
18-1	$La(PO_3)_3$	2960	0.16	−12.37	1.53	−10.79	111
18-2		2950	0.28	−11.69	1.87	−10.58	108
19-1	$60Ca(PO_3)_2\text{-}50Ga(PO_3)_3$	2980	0.36	−13.28	2.25	−12.39	125
19-2			0.10	−14.45	1.97	−12.45	129
20-1	$30Ca(PO_3)_2\text{-}70Ga(PO_3)_3$	2980	0.46	−13.91	2.24	−13.24	129
20-2		3000	0.20	−14.54	1.83	−13.14	130
21-1	$Ga(PO_3)_3$	3280	0.10	−17.63	0.08	−15.63	141
21-2	$33Ga_2O_3\text{-}67P_2O_5$	3300	0.36	−15.95	0.85	−15.06	134
			0.22	−16.24	0.15	−14.92	130
22-1	$40Ga_2O_3\text{-}60P_2O_5$	3340	0.40	−16.03	0.48	−15.23	132
23-1	$25BaO\text{-}75B_2O_3$	3470	0.32	−17.01	−2.83	−16.02	112
23-2			0.20	17.91	−3.17	−16.51	117
24-1	$30BaO\text{-}70B_2O_3$	3460	0.26	−16.76	−3.85	−15.59	103
24-2			0.22	−18.30	−2.84	−16.98	122
25-1	$35BaO\text{-}65B_2O_3$	3420	0.16	−17.83	0.41	−16.24	145
25-2		3410	0.20	−17.59	−1.61	−16.19	127

E (in kJ/mol) and the proton concentration $[H^+]$ for different glasses. For 45MgO-, 45CaO-, and $45BaO\text{-}55P_2O_5$ glasses, Eqs. (7), (8), and (9) were obtained, respectively:

$$E=110-12\log_{10}[H^+]\,, \tag{7}$$

$$E=101-14\log_{10}[H^+]\,, \tag{8}$$

$$E=95-16\log_{10}[H^+]\,. \tag{9}$$

Thus, E is assumed to be expressed by

$$E=E_0+E_1\,, \tag{10}$$

where E_0 is an activation energy at a unit concentration of the proton ($[H^+]=1$), and E_1 is an activation energy depending on carrier concentration. Figure 4 shows a plot of E_0 against ν_{OH}; E_0 increases linearly with increasing ν_{OH}. It was found experimentally that E_0 is expressed by Eq. (11) and E_1 by Eq. (12), respectively,

$$E_0=B_0+B_1\nu_{OH}\,, \tag{11}$$

$$E_1=-B_2\log_{10}[H^+]\,, \tag{12}$$

where B_0, B_1 are a constant ($B_0=-66$, $B_1=5.89\times10^{-2}$) and B_2 is a value depending on host-glass compositions. The protonic conduction process is considered to be controlled by the two elemental process, i.e., one is a bond-breaking process between oxygen and proton in O—H bonding, and the other is a jumping or transporting process from a given site to a next site. We assume that E_0 is related to the former process and E_1 is to the latter process. These discussion will be done in another paper in detail.

It is very convenient and significant to be able to evaluate the proton conductivity and the activation energy of a glass simultaneously by measuring an ir spectrum of a given glass plate.

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